

## 2.5 Surface-Altered Zeolites as Permeable Barriers for In Situ Treatment of Contaminated Groundwater

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### Abstract

The current research focuses on enhanced removal of mobile metals and chlorinated hydrocarbons from contaminated water by a combination of a reduction material (represented by zero valent iron, ZVI) and a sorption material (represented by surfactant-modified zeolite, SMZ). Natural zeolite and ZVI were homogenized and pelletized to maintain favorable hydraulic properties while minimizing material segregation due to bulk density differences. The zeolite/ZVI pellets were modified with the cationic surfactant hexadecyltrimethylammonium bromide to increase contaminant sorption and, thus, the contaminant concentration on the solid surface. The chromate and perchloroethylene (PCE) degradation rates with and without surfactant modification were determined separately. The pseudo first-order reduction rate constant increased by a factor of nine for chromate and by a factor of three for PCE following surfactant modification. The enhanced contaminant reduction capacity of SMZ/ZVI pellets should allow a decrease in the amount of material required to achieve a given level of contaminant removal, while the highly porous pellets will help maintain favorable hydraulic properties in subsurface permeable barriers. Predictions based on results of the laboratory experiments indicated that chromate concentrations would be reduced below detectable levels in a 1-m-thick SMZ/ZVI barrier, while PCE levels would be reduced by four orders of magnitude.

The performance of the pellets at the pilot scale was tested in an experimental aquifer facility at the Oregon Health and Science University. The University of Dayton Research Institute prepared approximately 13 m<sup>3</sup> of SMZ/ZVI pellets for the pilot test.

The pellets were installed in a 6-m long by 2-m wide by 2-m deep subsurface permeable barrier in a 10-m by 10-m by 3-m deep simulated aquifer. In a five-week test, a plume of  $6000 \mu\text{g L}^{-1}$  of chromate and  $500 \mu\text{g L}^{-1}$  of PCE was injected into the pilot test tank. At the end of the test, chromate concentrations down gradient of the barrier were nondetectable; PCE concentrations had been reduced by about two orders of magnitude. The plume was fully captured, with no bypass under or around the barrier, indicating that the desired hydraulic conductivity contrast between the barrier and aquifer material was maintained during the test. The less than expected reduction in PCE concentrations appeared due to variability in the bulk-produced pellets manufactured for the pilot test. Refinements in the bulk-production process should create a pellet with significantly enhanced contaminant reduction characteristics, along with improved hydraulic properties, compared to other candidate permeable barrier materials.

# **Surface-altered Zeolites As Permeable Barriers for in Situ Treatment of Contaminated Groundwater**

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***New Mexico Institute of Mining and Technology***

**Richard L. Johnson and Timothy L. Johnson**

***Oregon Graduate Institute***

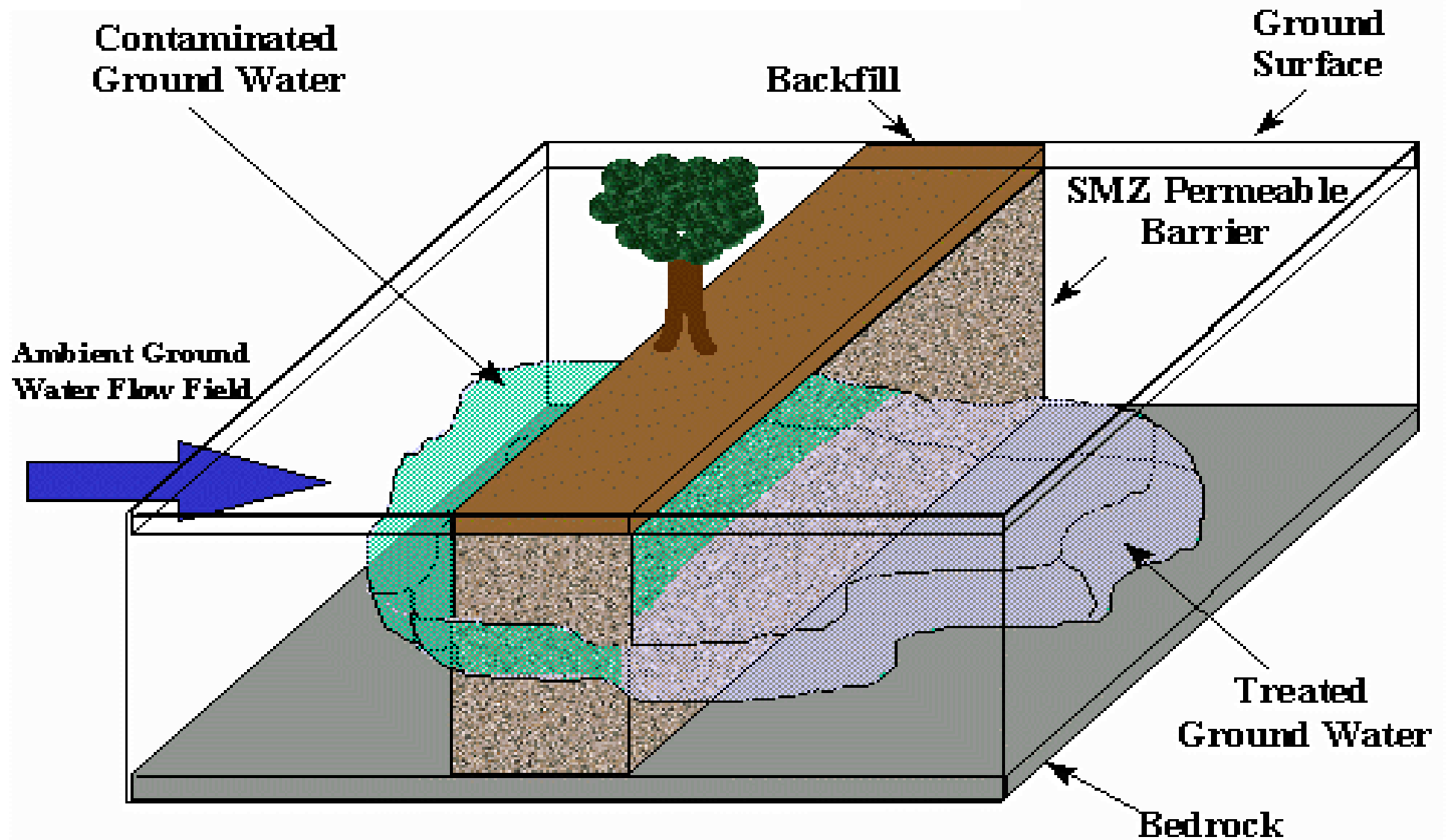
**Douglas Wolf**

***University of Dayton Research Institute***

**Supported by Contract No. DE-AR21-95MC32108**

**National Energy Technology Laboratory**

# Permeable Barrier



# Outline

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## PREVIOUS PROJECT PHASES

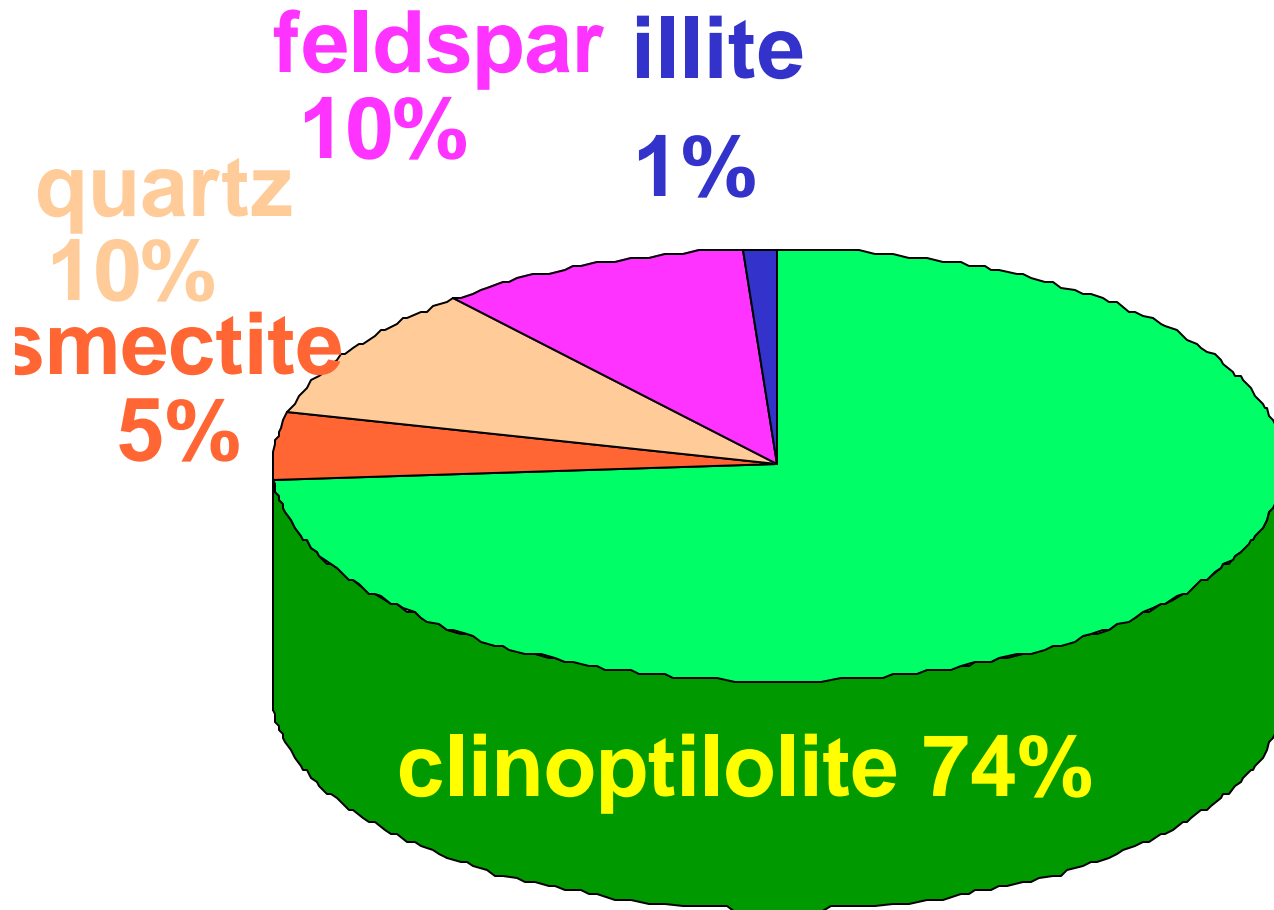
- Development of SMZ
- Pilot testing of SMZ

## CURRENT PROJECT PHASE

- Development of SMZ/ZVI pellets
- Lab testing of SMZ/ZVI pellets
- Pilot testing of SMZ/ZVI pellets
- Project schedule

# Zeolite Properties

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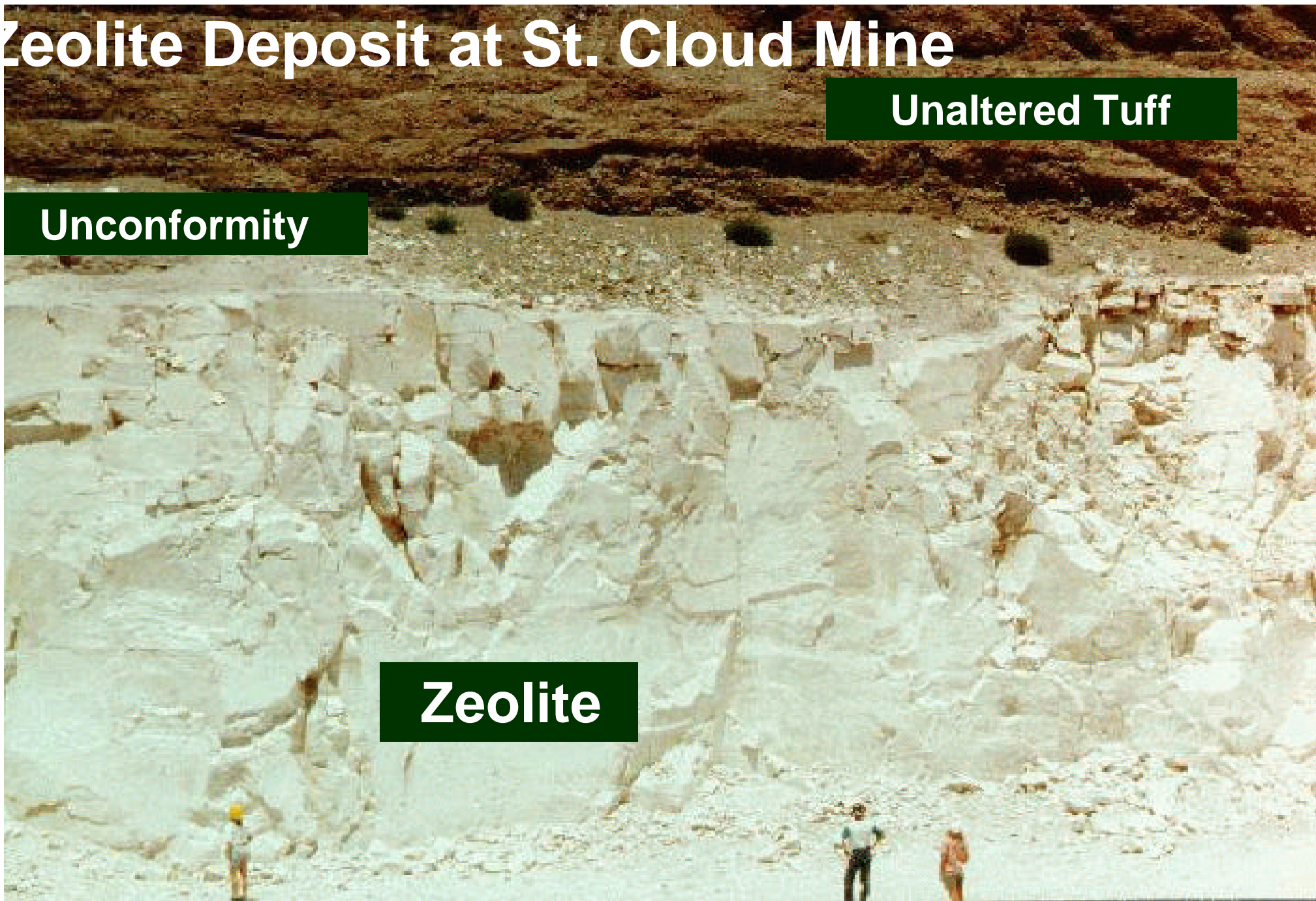
- High surface area
- High internal and external cation exchange capacity
- Can be tailored to any particle size/permeability

# Zeolite Deposit at St. Cloud Mine

Unaltered Tuff

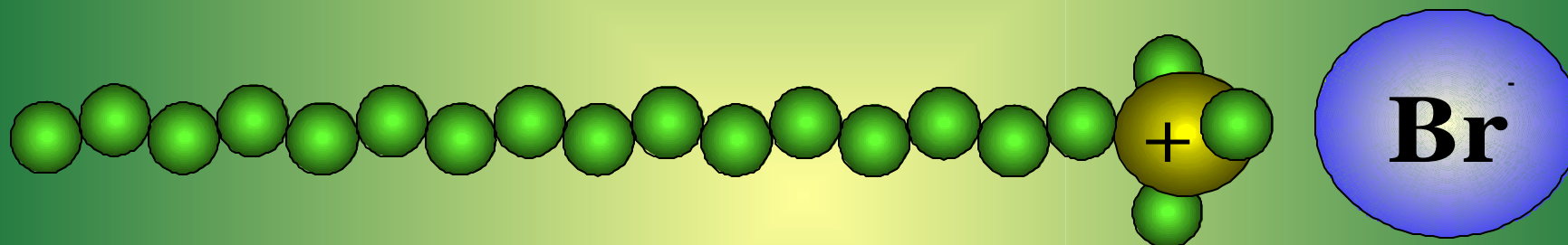
Unconformity

Zeolite



# HDTMA - A Cationic Surfactant

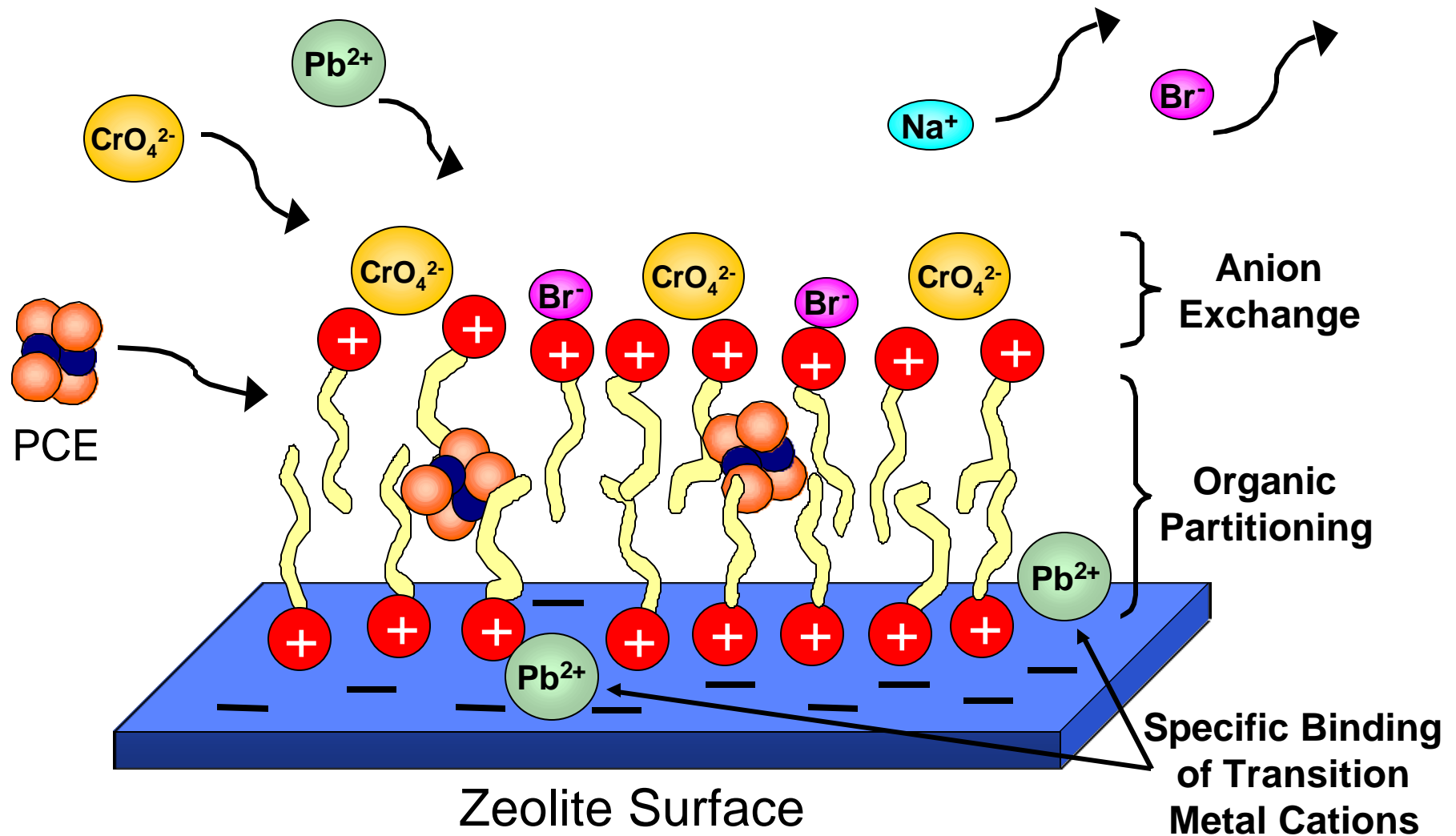
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**Hexadecyltrimethylammonium Bromide**



# SMZ Retention Mechanisms



# Outline

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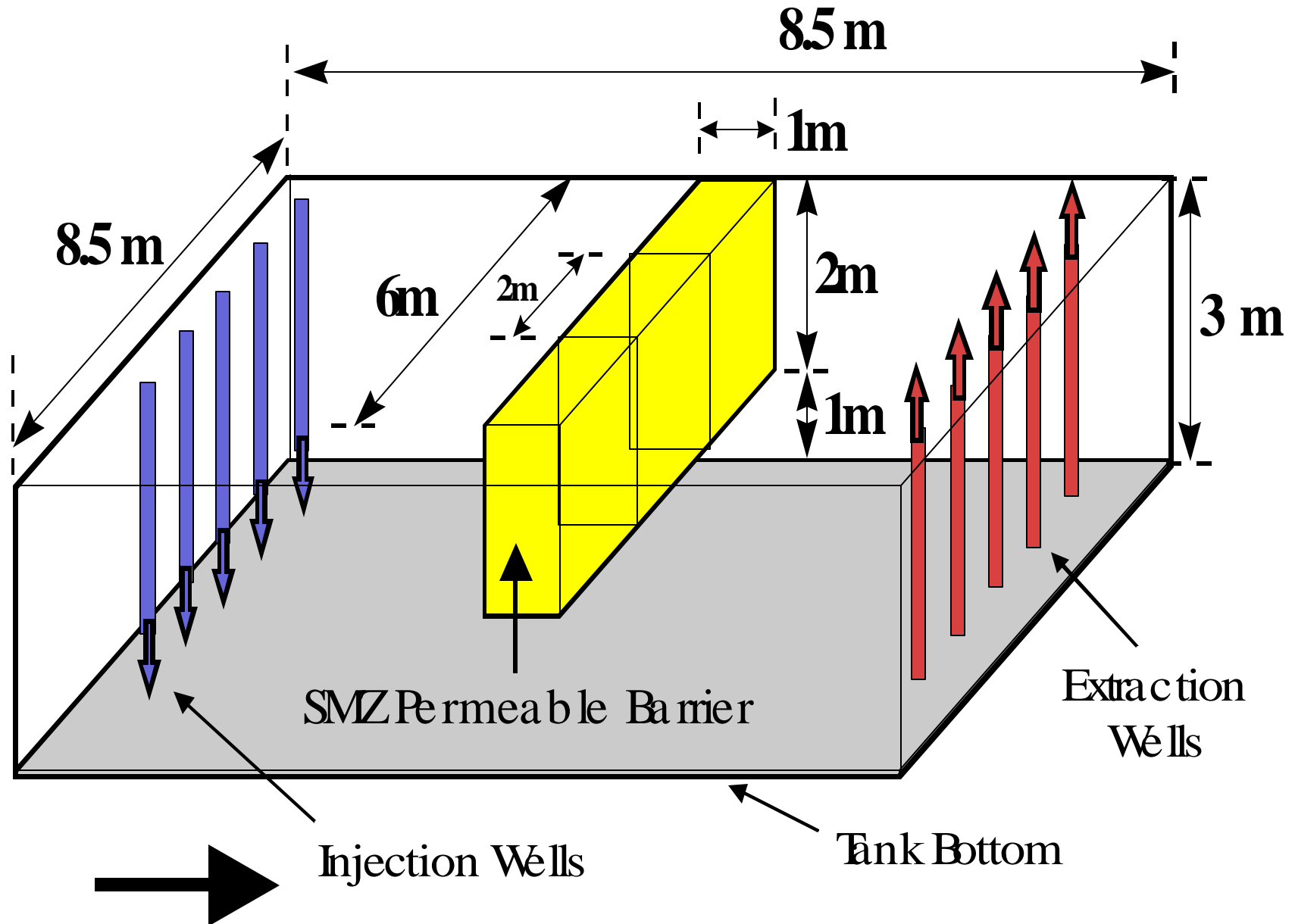
## PREVIOUS PROJECT PHASES

- Development of SMZ
- Pilot testing of SMZ

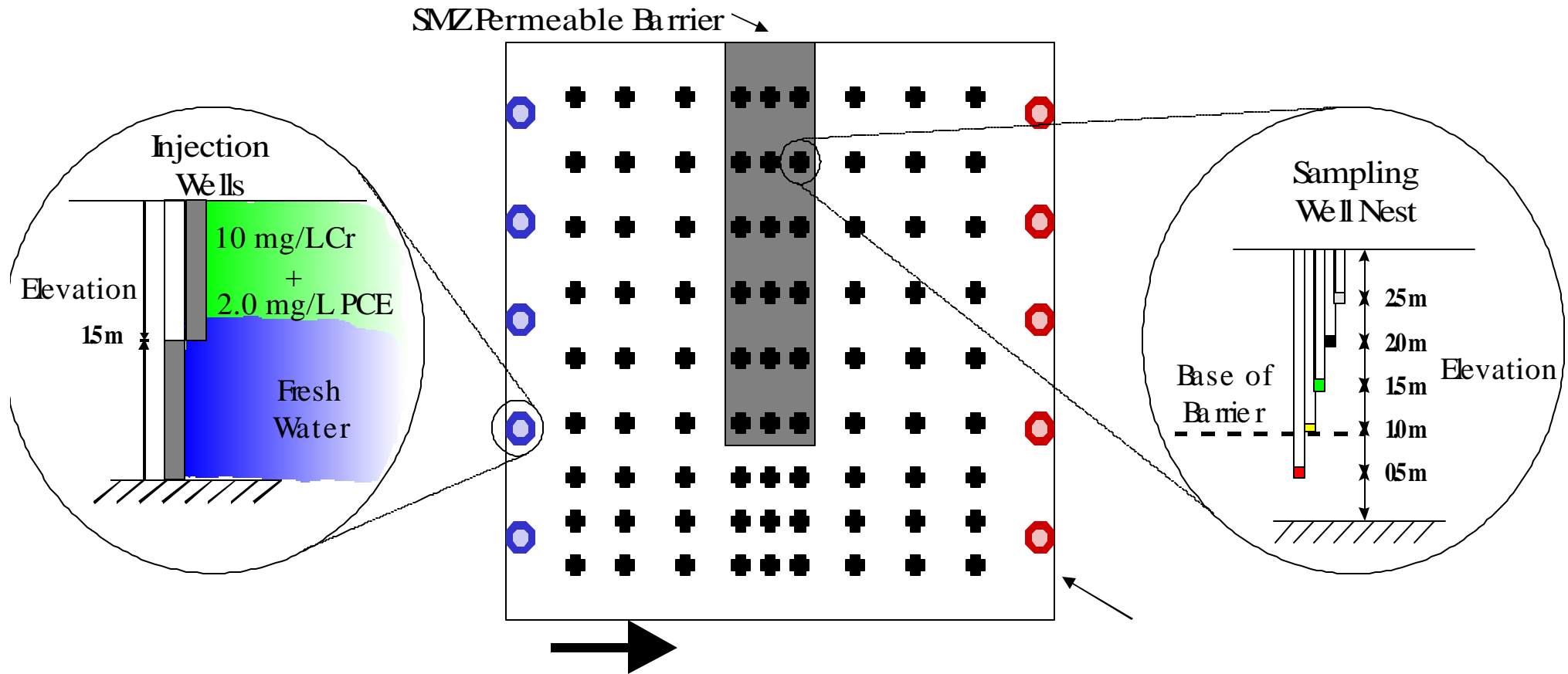
## CURRENT PROJECT PHASE

- Development of SMZ/ZVI pellets
- Lab testing of SMZ/ZVI pellets
- Pilot testing of SMZ/ZVI pellets
- Project schedule

# Pilot Scale Study Tank at OGI



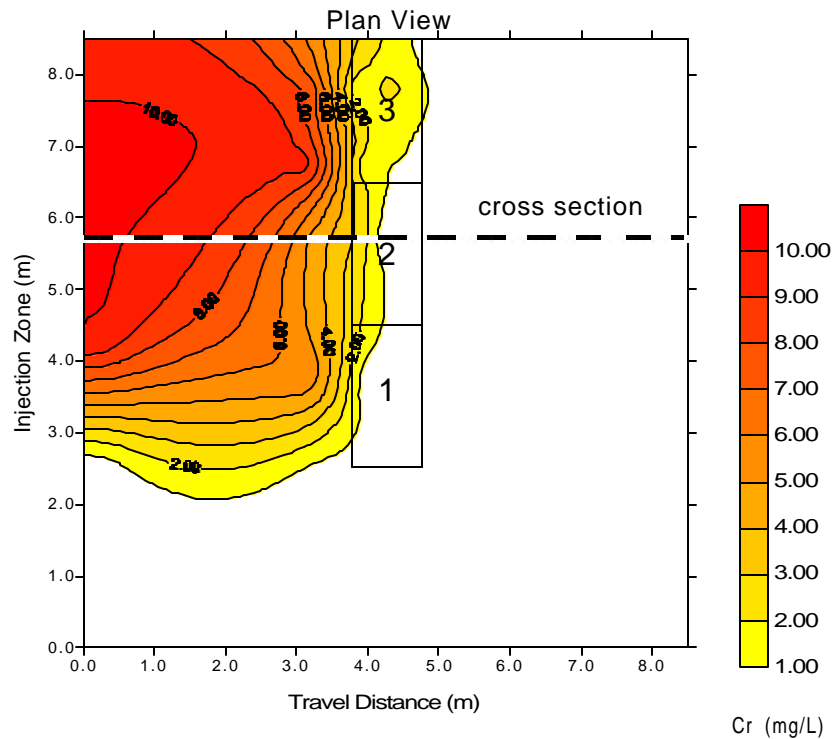
# Sample Well Locations



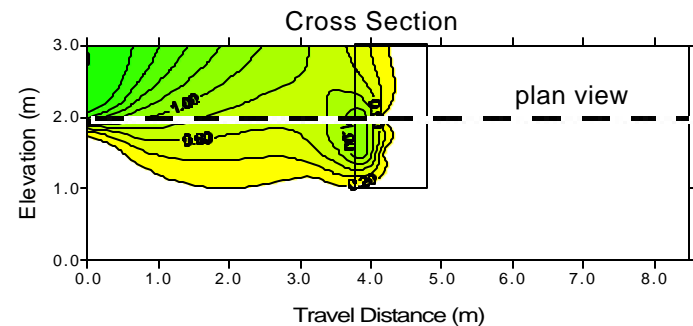
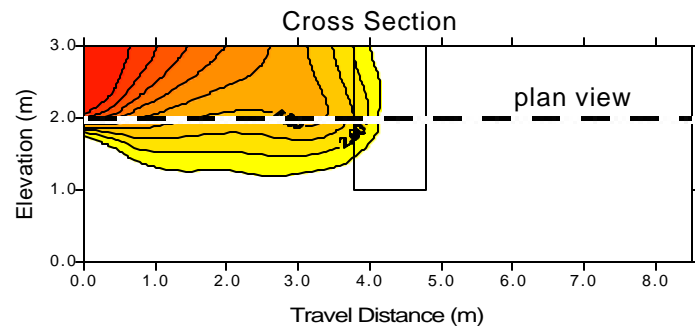
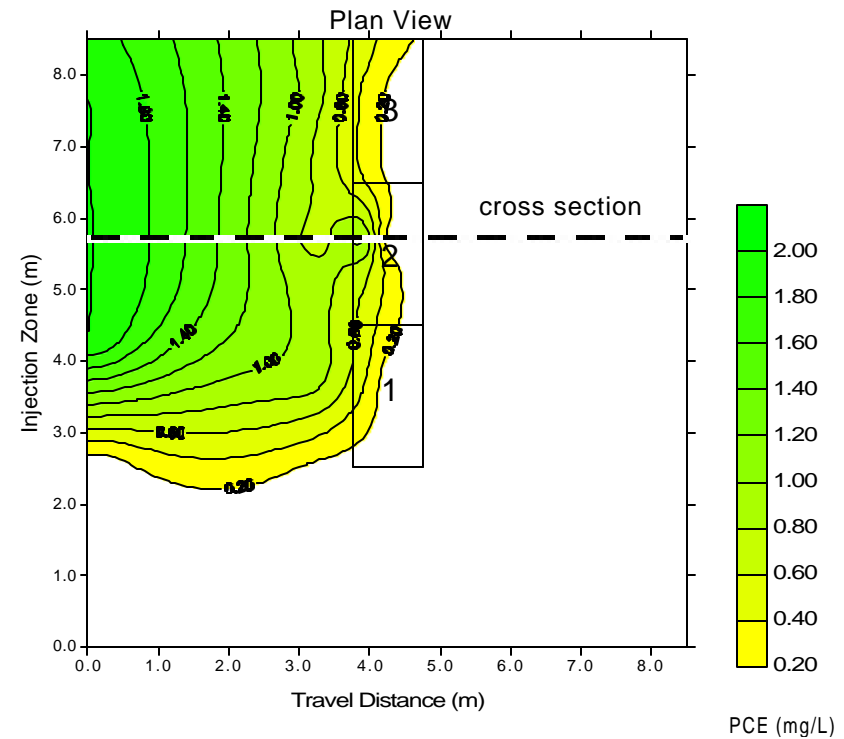


# Cr and PCE Distributions, Day 41

Cr Distribution after 41 days of injection (8/20/98)



PCE Distribution after 41 days of injection (8/20/98)



# Pilot Test R vs. Lab R

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	PCE	CrO <sub>4</sub> <sup>2-</sup>
Retardation Factor	$R = 1 + \frac{rK_D}{q}$	$R = 1 + \frac{rK_L b}{q(1 + K_L C)}$ (assuming C=10 mg L <sup>-1</sup> )
Lab R	29	42
Pilot Test R	39	44

# Outline

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## PREVIOUS PROJECT PHASES

- Development of SMZ
- Pilot testing of SMZ

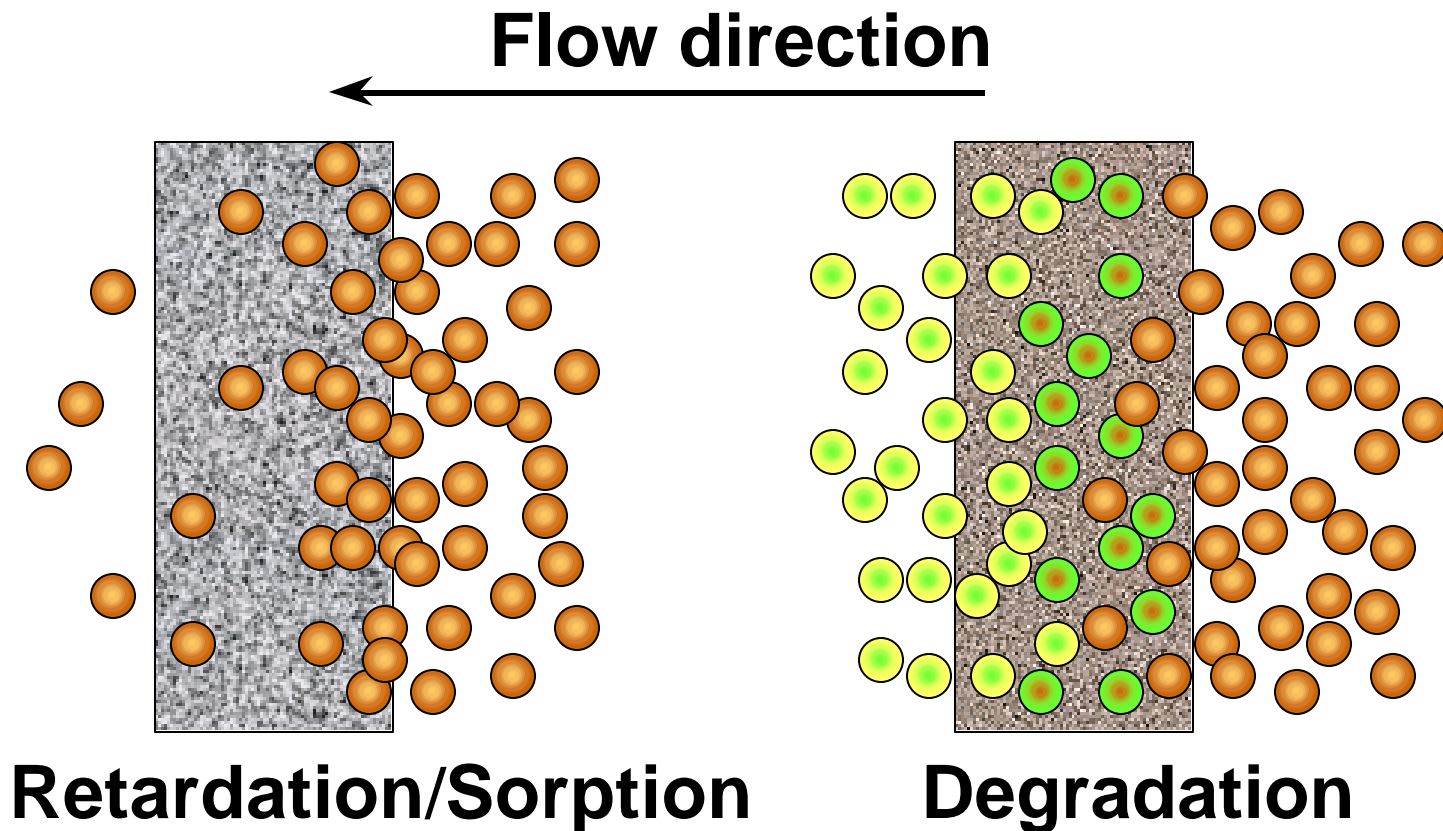
## CURRENT PROJECT PHASE

- Development of SMZ/ZVI pellets
- Lab testing of SMZ/ZVI pellets
- Pilot testing of SMZ/ZVI pellets
- Project schedule



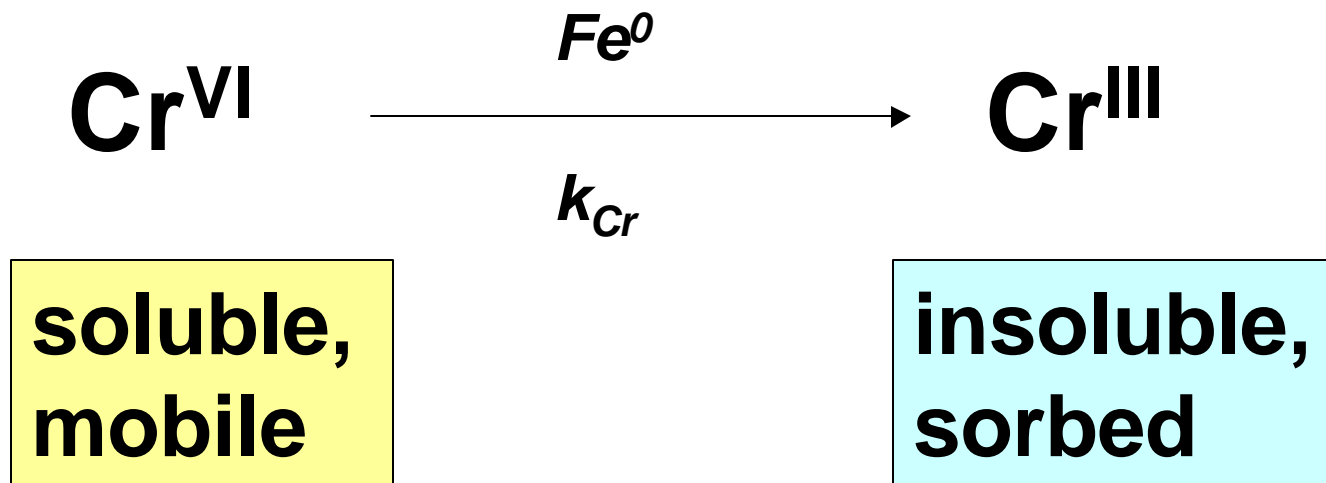
# Permeable Barriers Types

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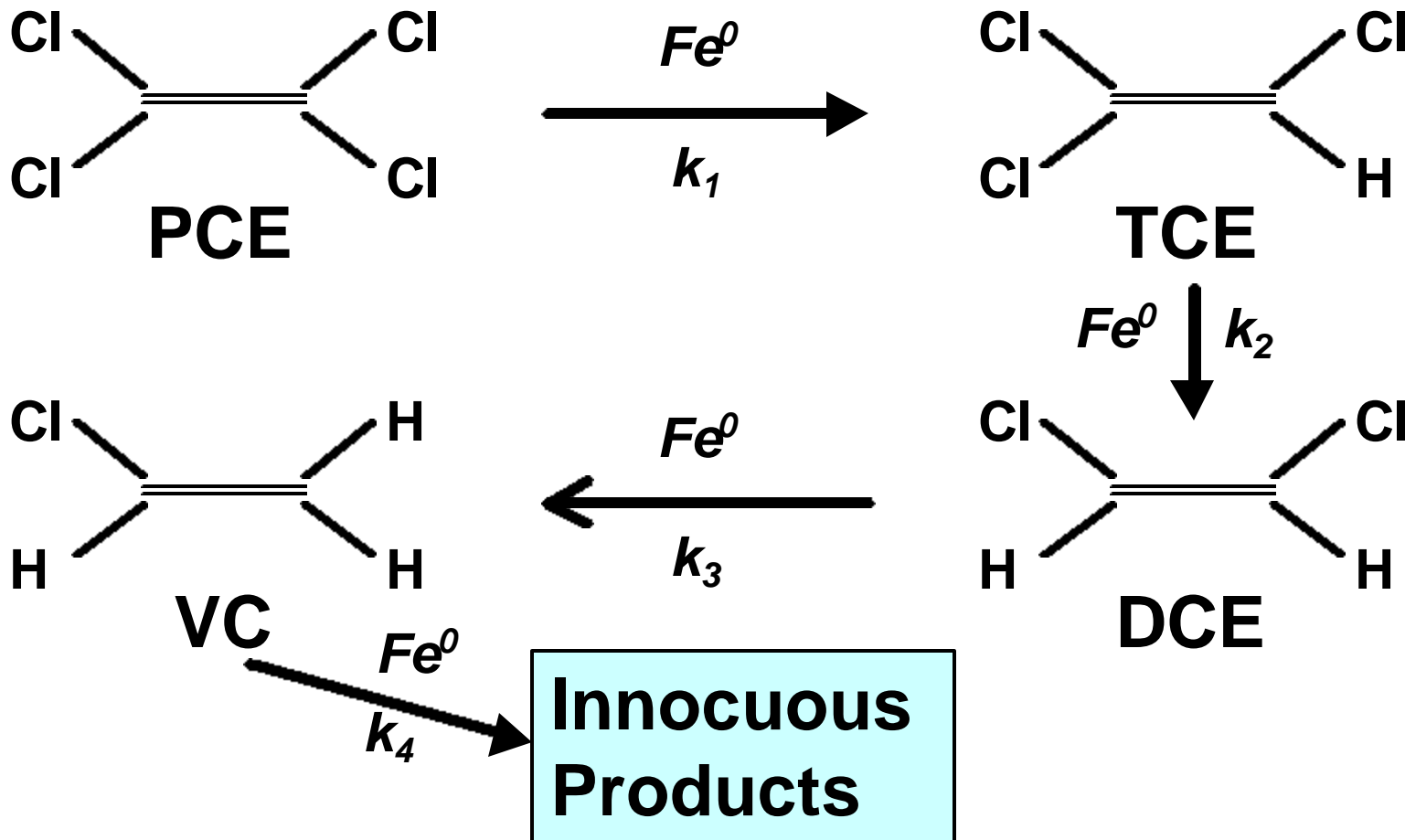


# Chromate Reduction by ZVI

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# Chlorinated HC Reduction by ZVI

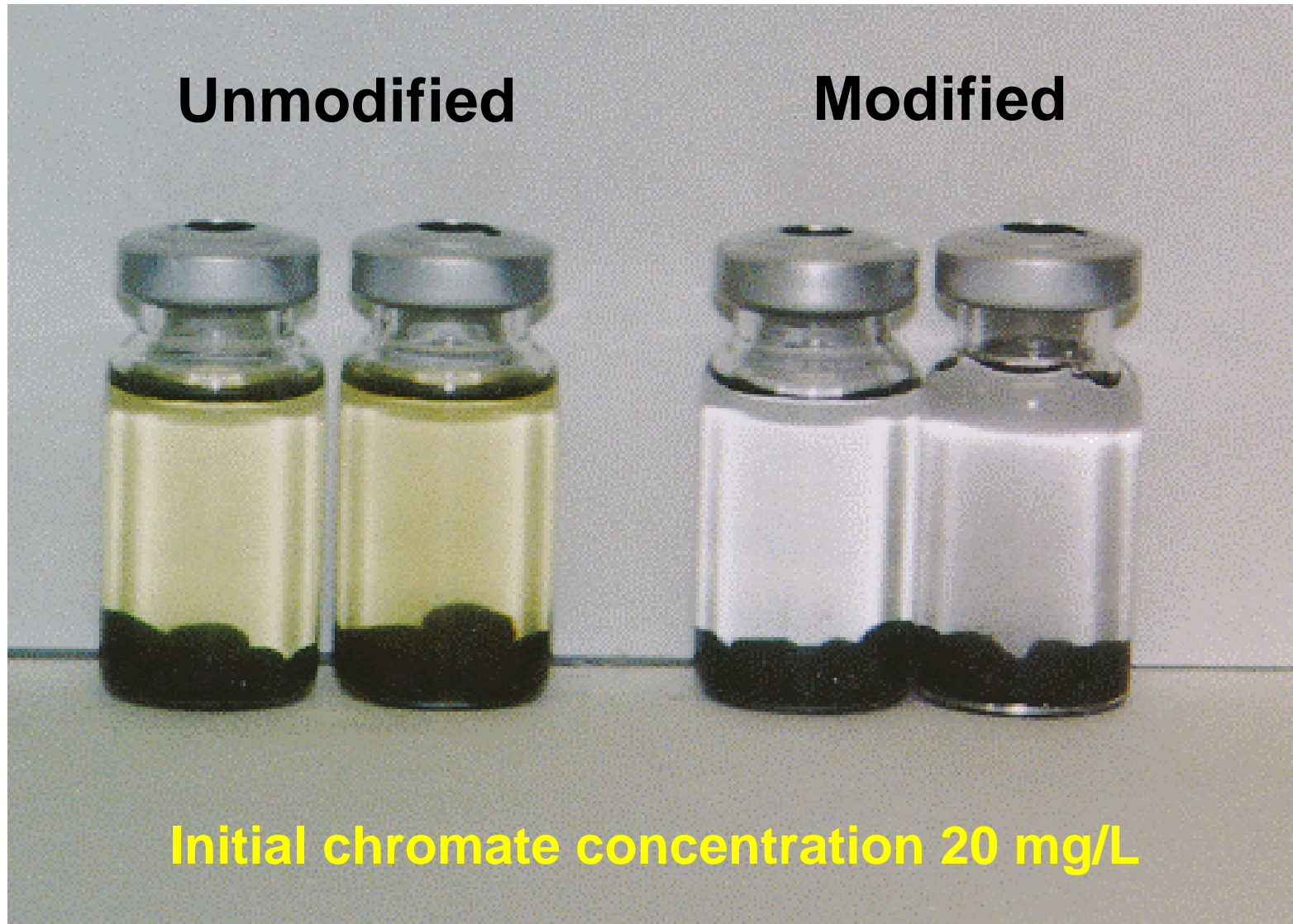


# SMZ/ZVI Pellets

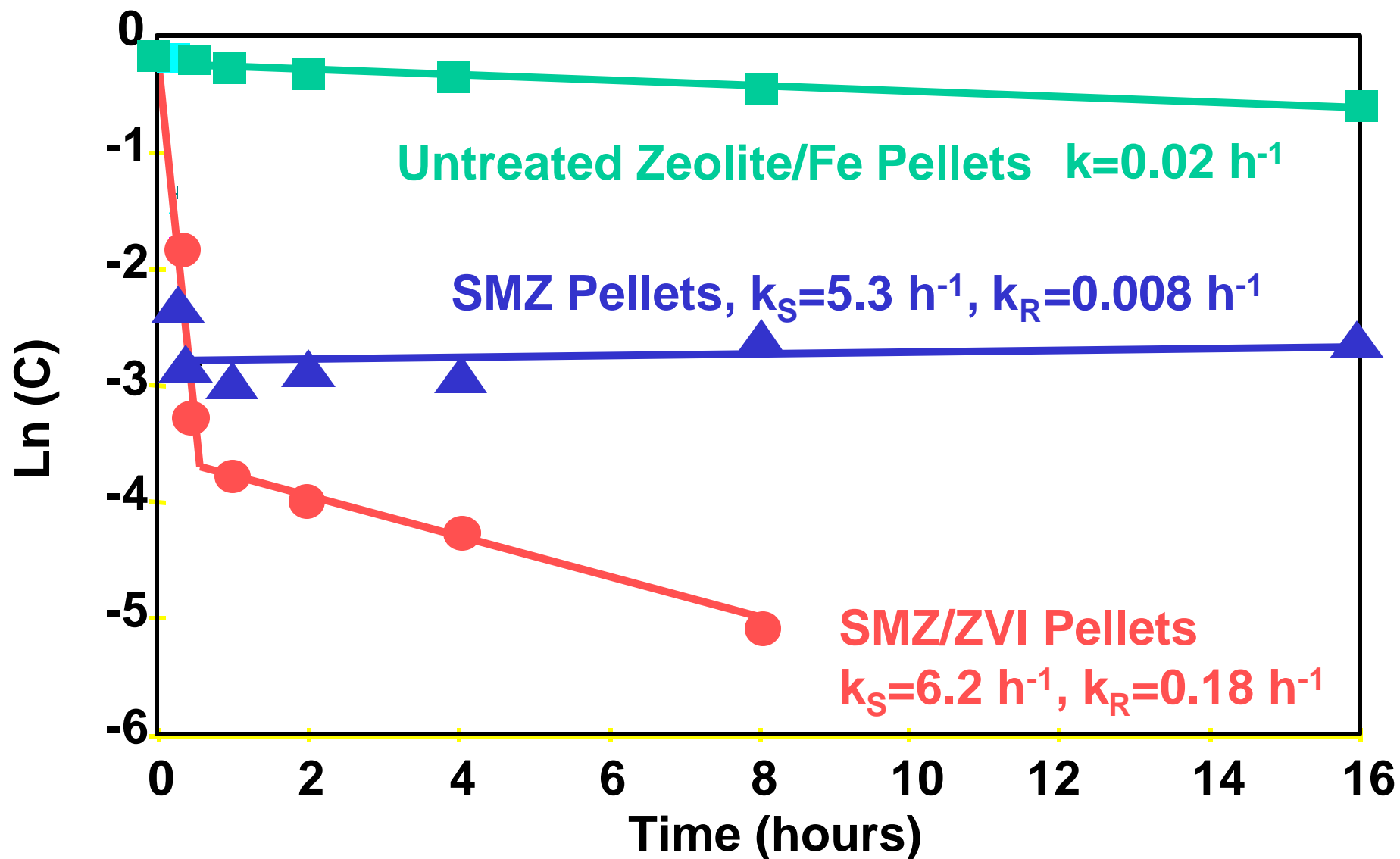
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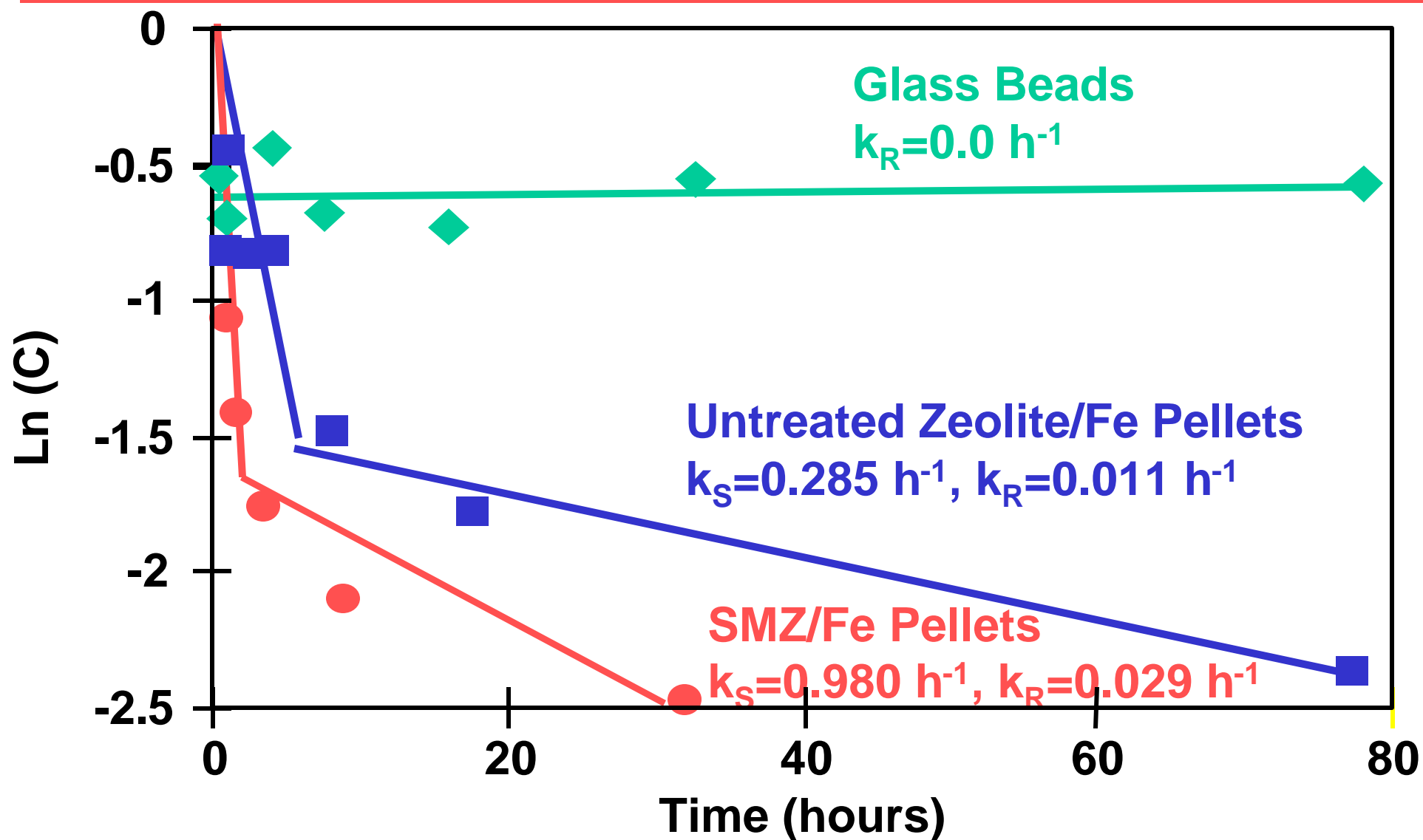
# Cr (VI) Sorption/Reduction by SMZ/ZN



# Chromate Reduction Kinetics

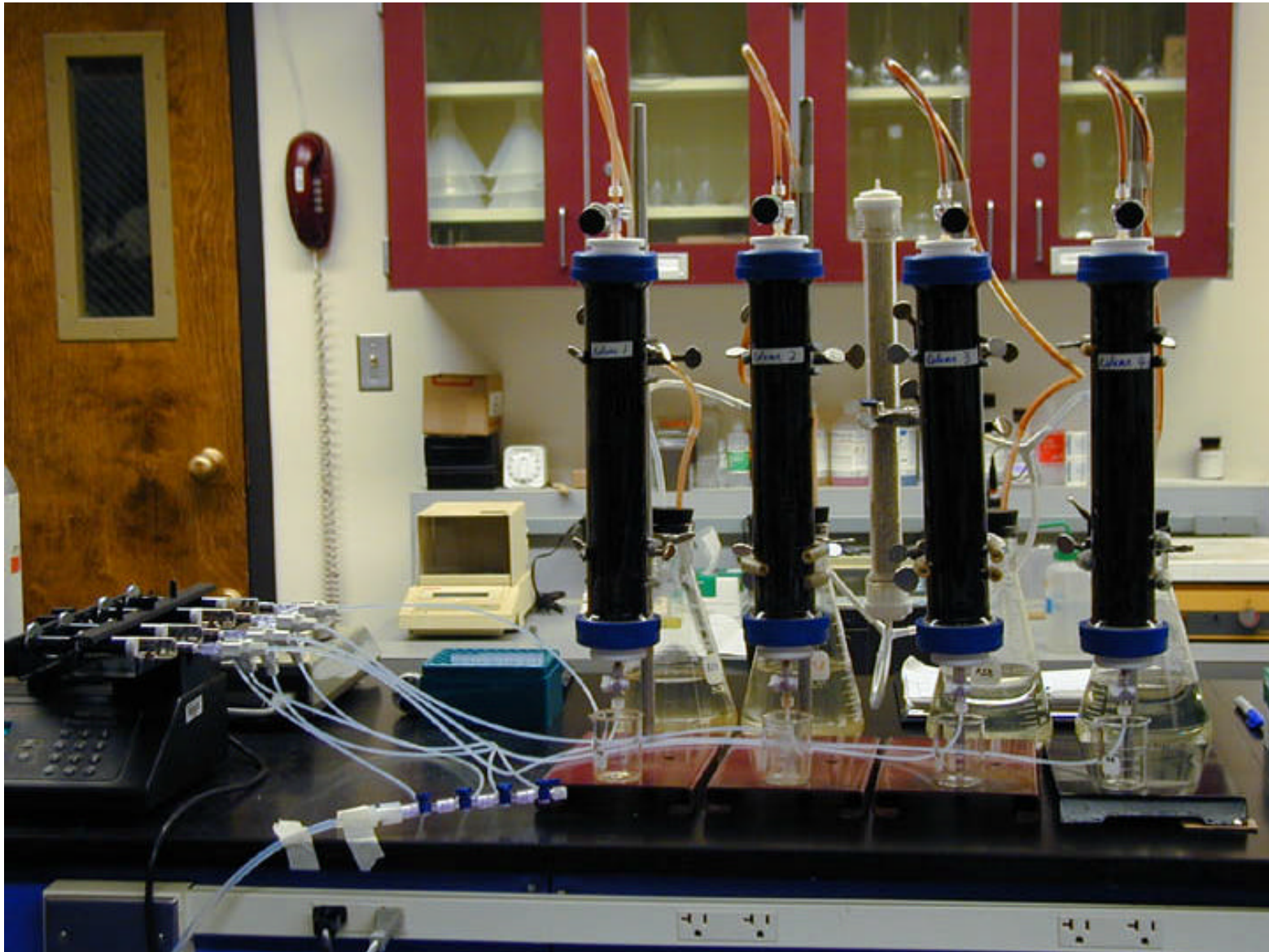


# PCE Reduction Kinetics



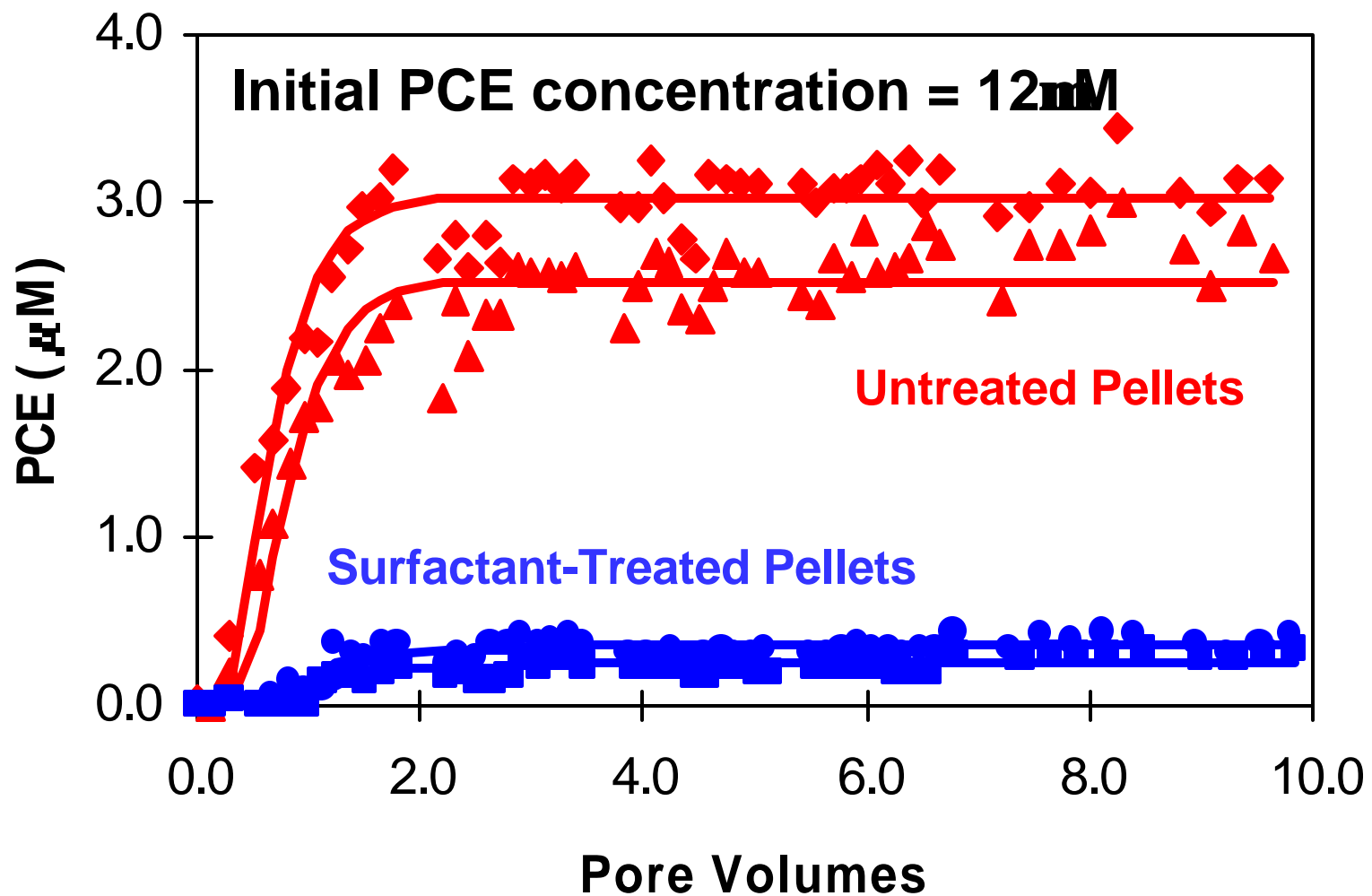
# SMZ/ZVI Testing in Lab Columns

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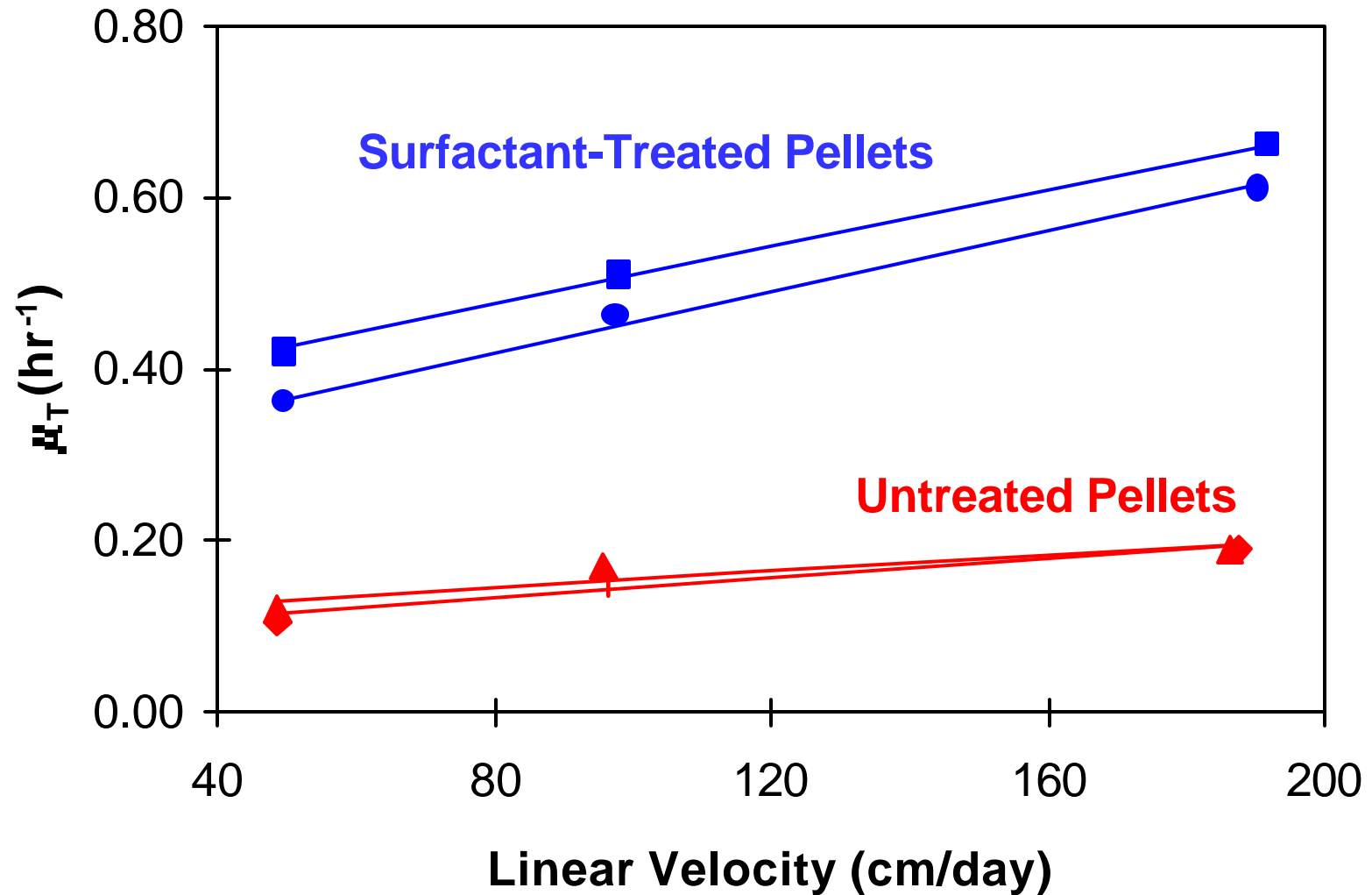


# PCE Reduction by Fe/SMZ



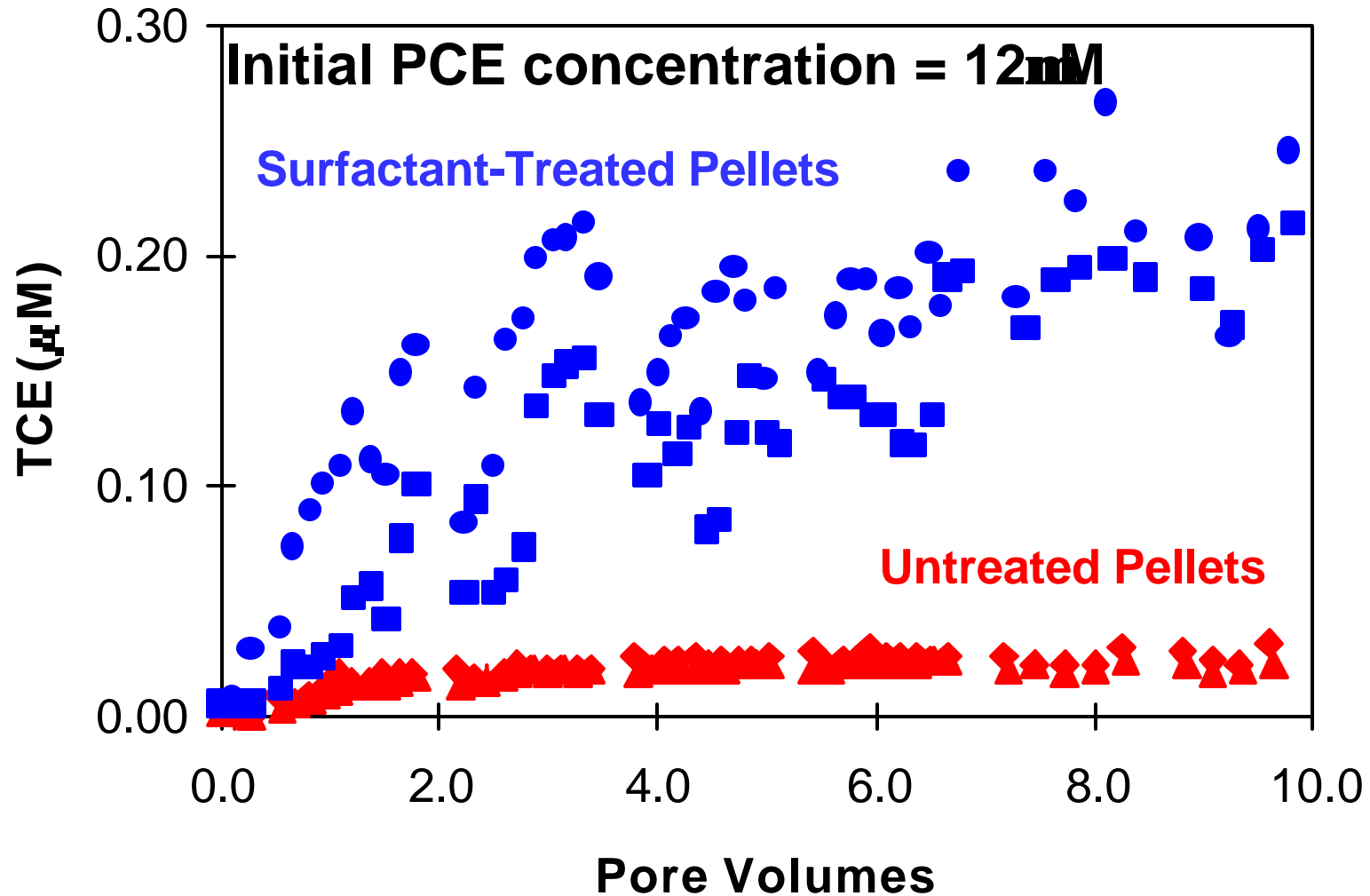
# PCE Reduction Rate vs. Velocity

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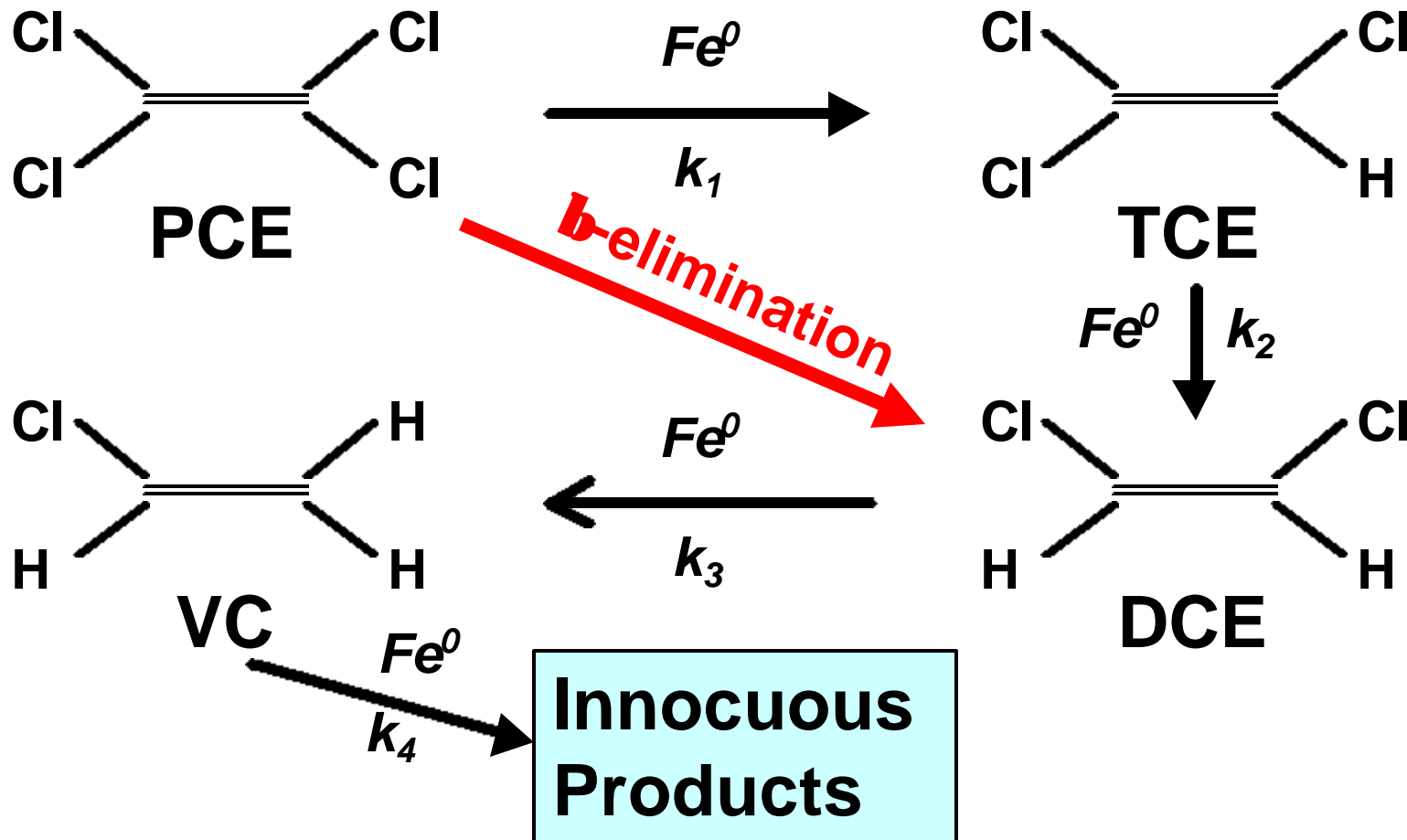


# TCE Produced from PCE Reduction

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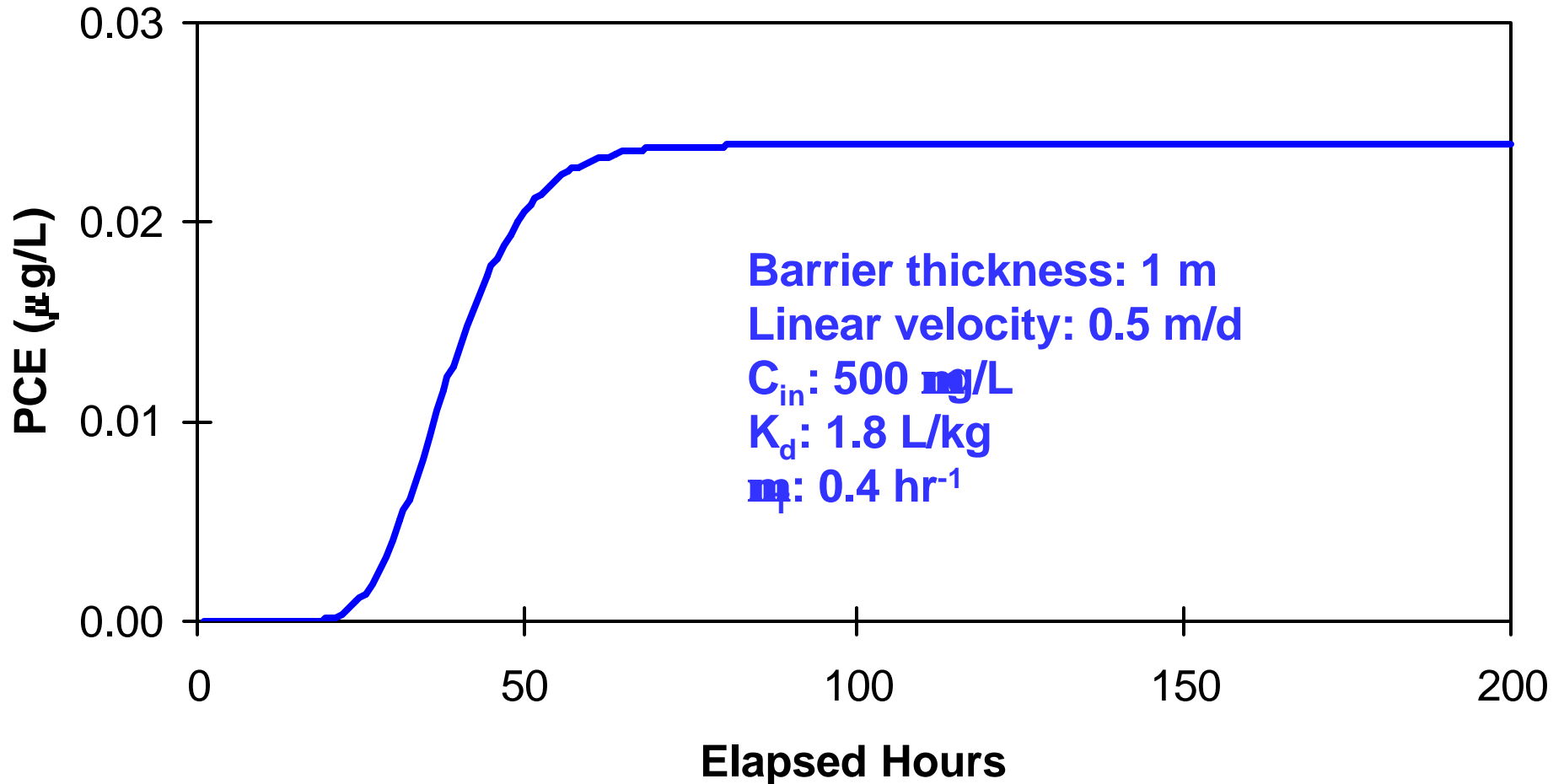


# Chlorinated HC Reduction



# PCE Breakthrough in SMZ/ZVI Barriers

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# Outline

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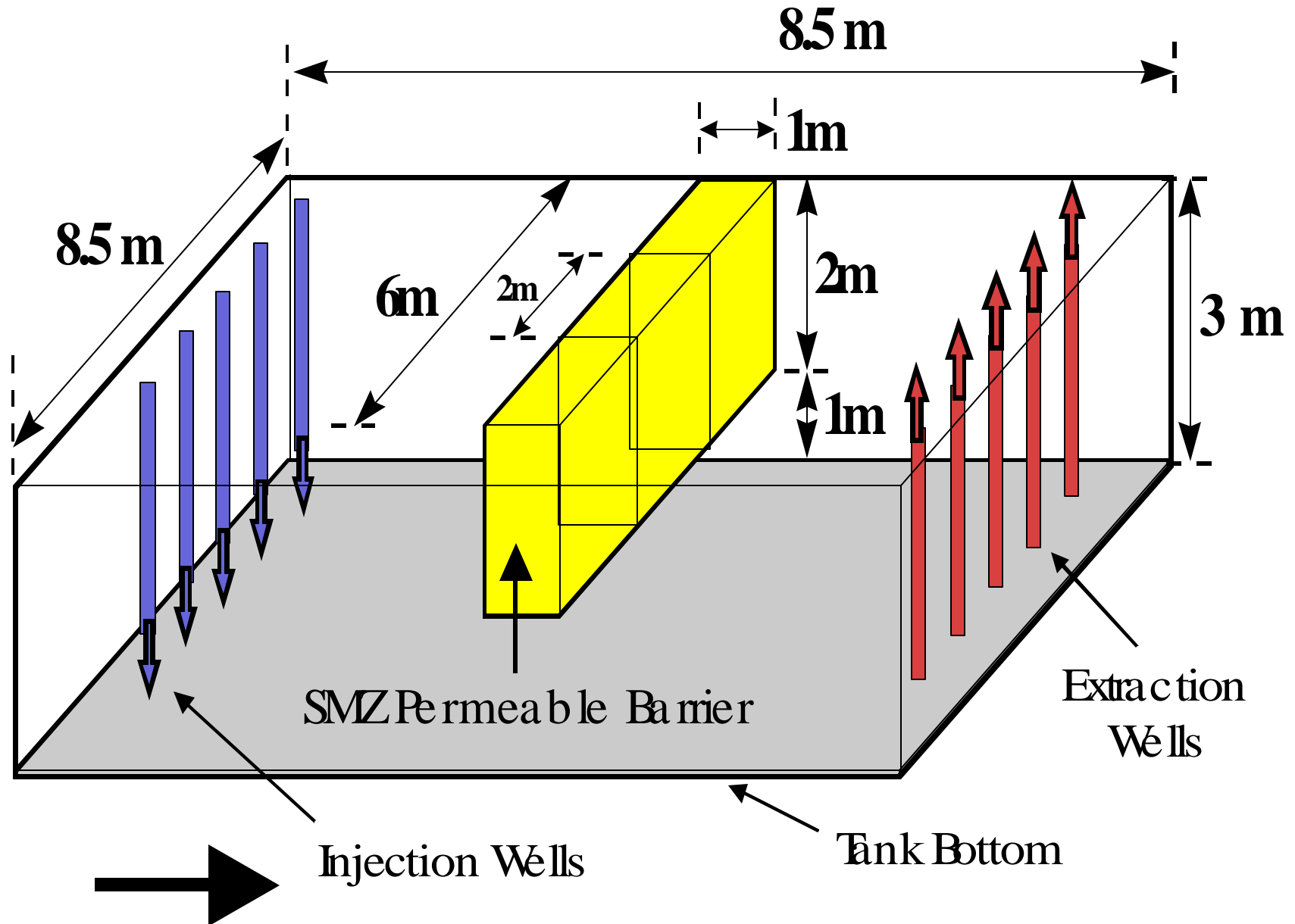
## PREVIOUS PROJECT PHASES

- Development of SMZ
- Pilot testing of SMZ

## CURRENT PROJECT PHASE

- Development of SMZ/ZVI pellets
- Lab testing of SMZ/ZVI pellets
- Pilot testing of SMZ/ZVI pellets
- Project schedule

# Pilot Scale Study Tank at OGI



# SMZ/ZVI Cubes in Barrier

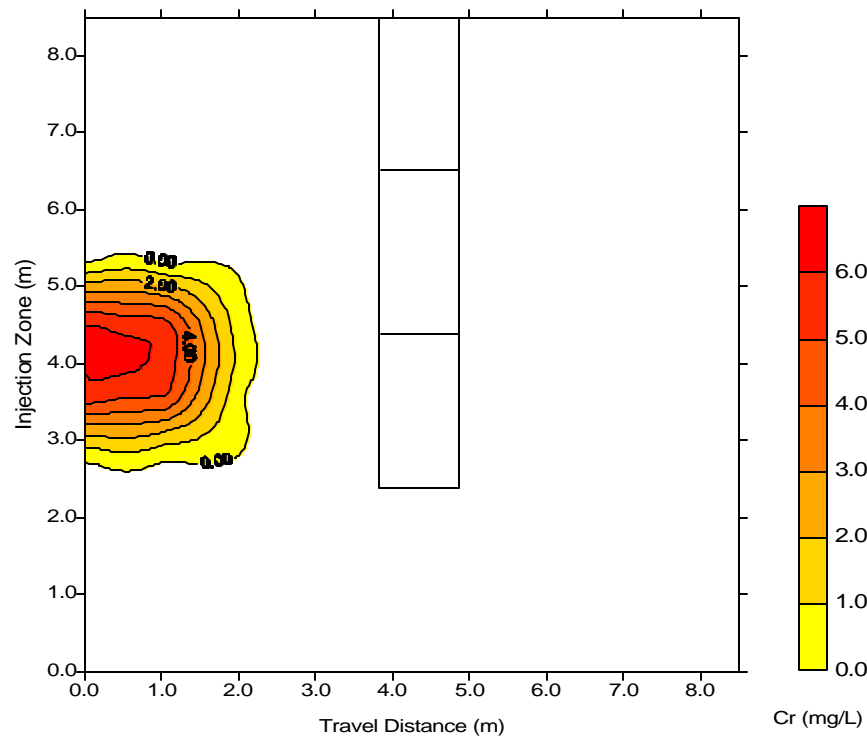
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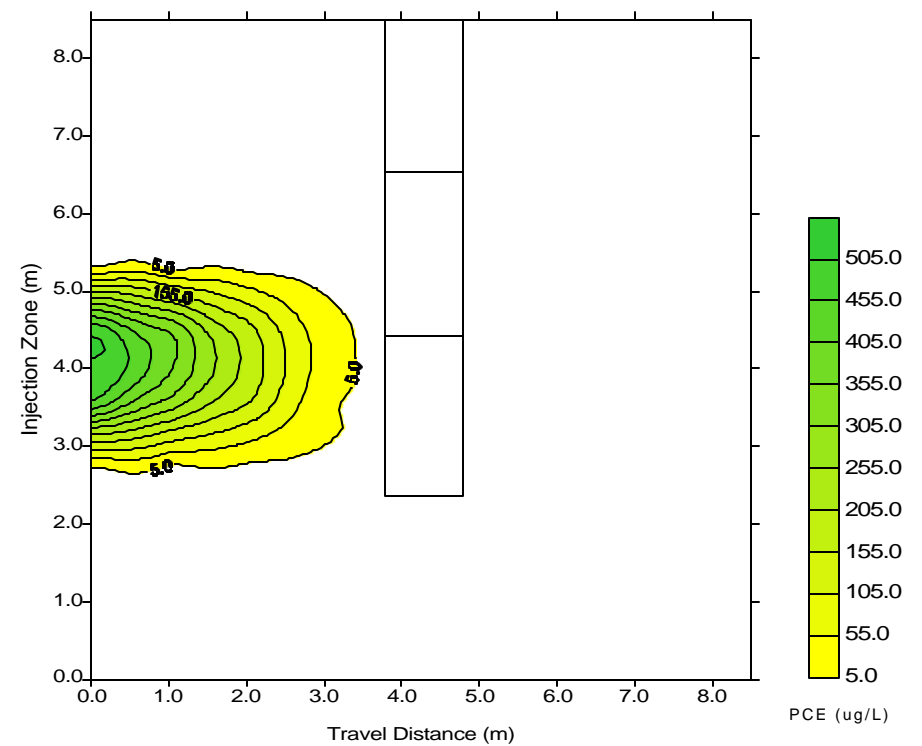


# Cr and PCE Distributions, 1<sup>st</sup> week

Cr Distribution after 3 days of injection (7/02/2001)  
Depth=1.0m  
Plan View

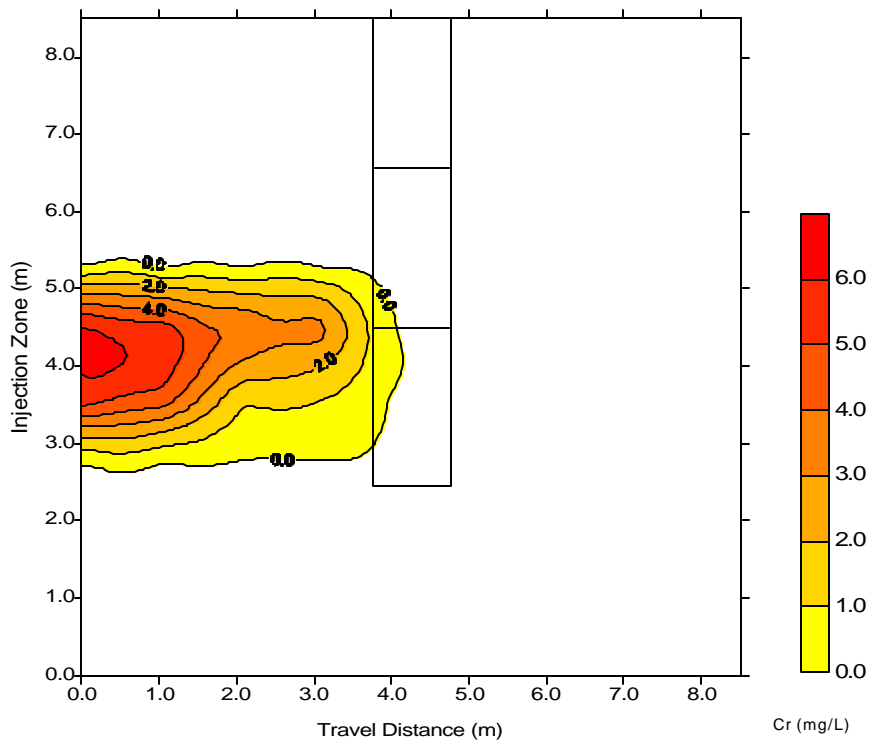


PCE Distribution after 6 days of injection (7/02/2001)  
Depth=1.0m  
Plan View

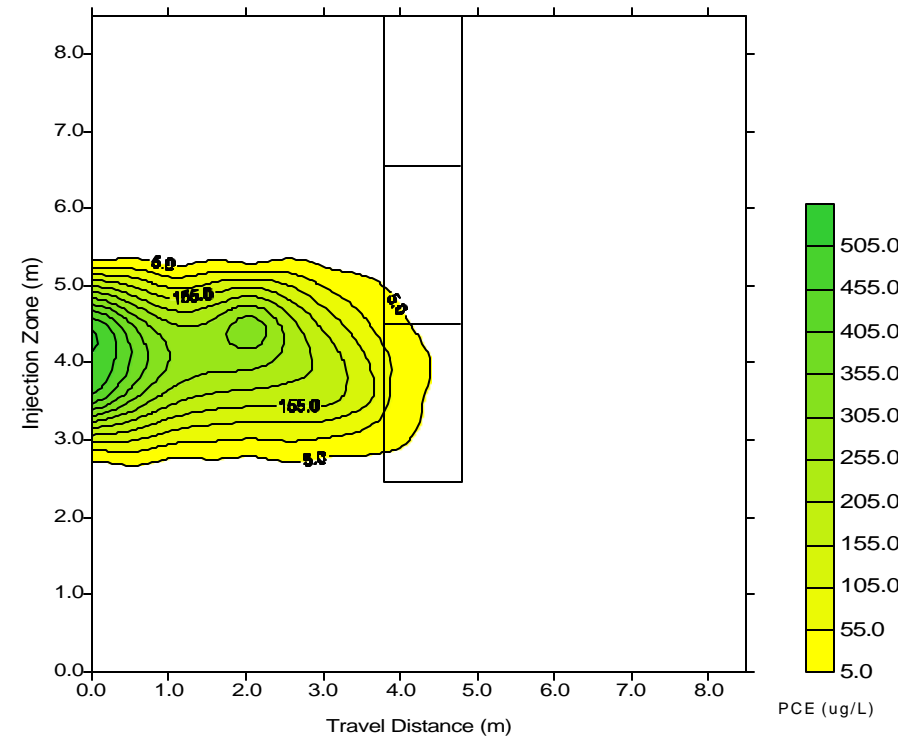


# Cr and PCE Distributions, 2<sup>nd</sup> week

Cr Distribution after 12 days of injection (7/11/2001)  
Depth=1.0m  
Plan View

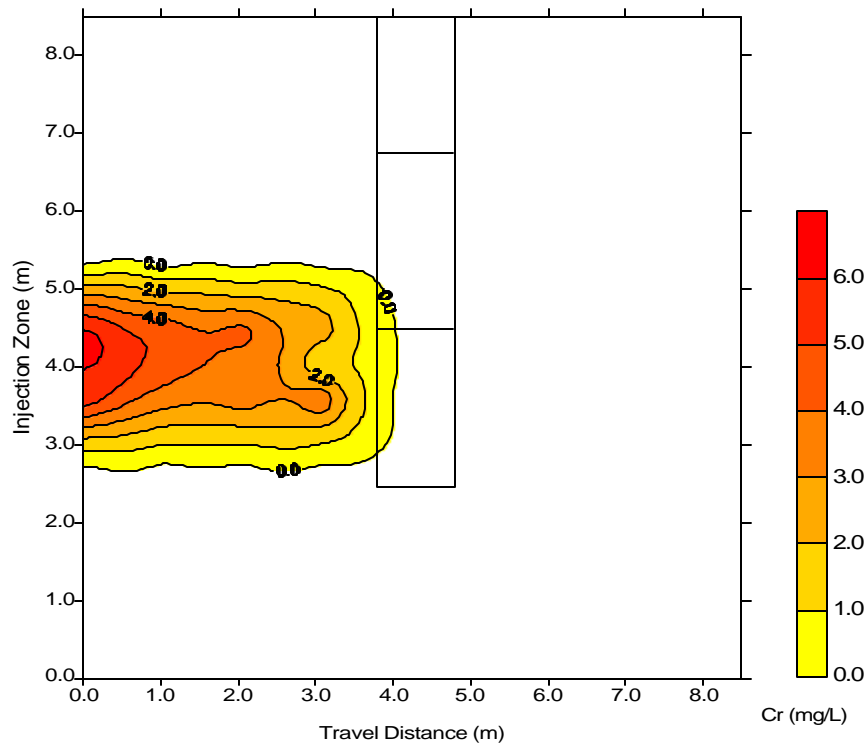


PCE Distribution after 15 days of injection (7/11/2001)  
Depth=1.0m  
Plan View

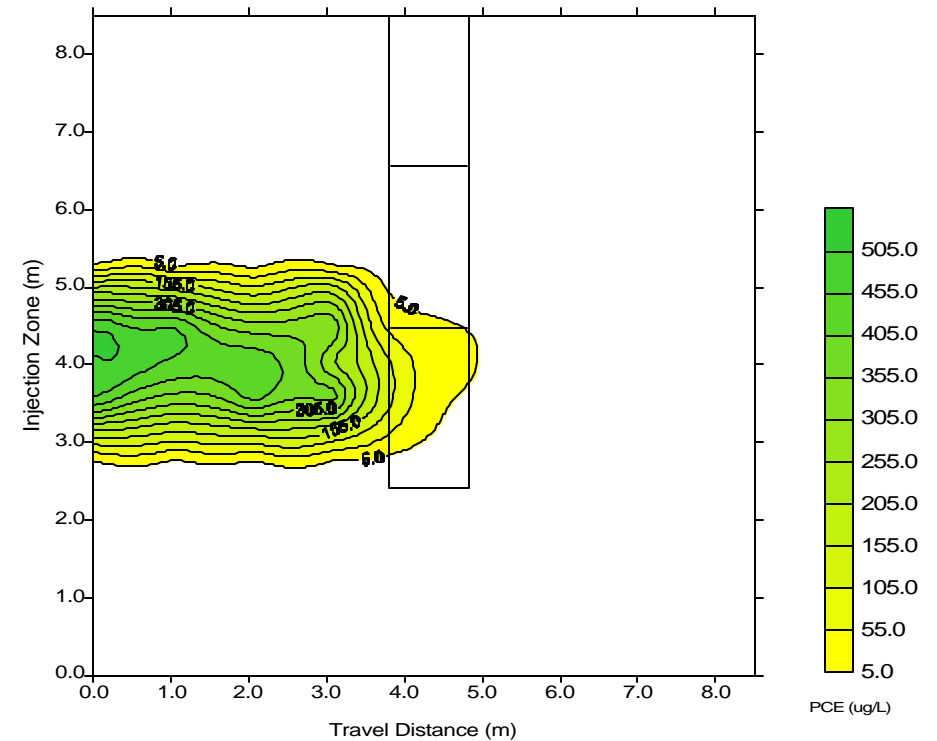


# Cr and PCE Distributions, 3<sup>rd</sup> week

Cr Distribution after 19 days of injection (7/18/2001)  
Depth=1.0m  
Plan View

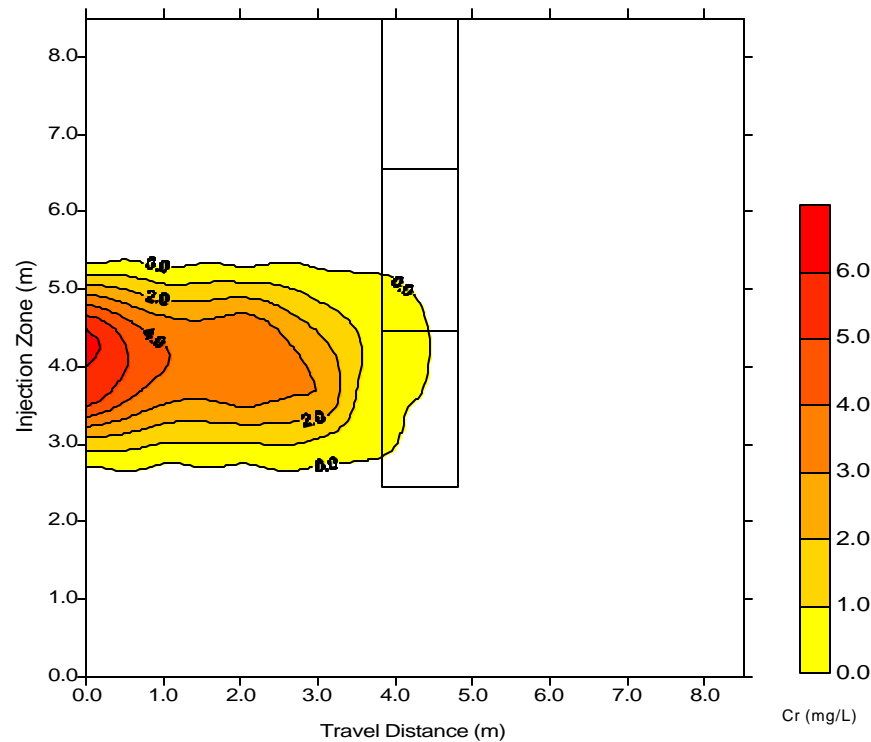


PCE Distribution after 22 days of injection (7/18/2001)  
Depth=1.0m  
Plan View

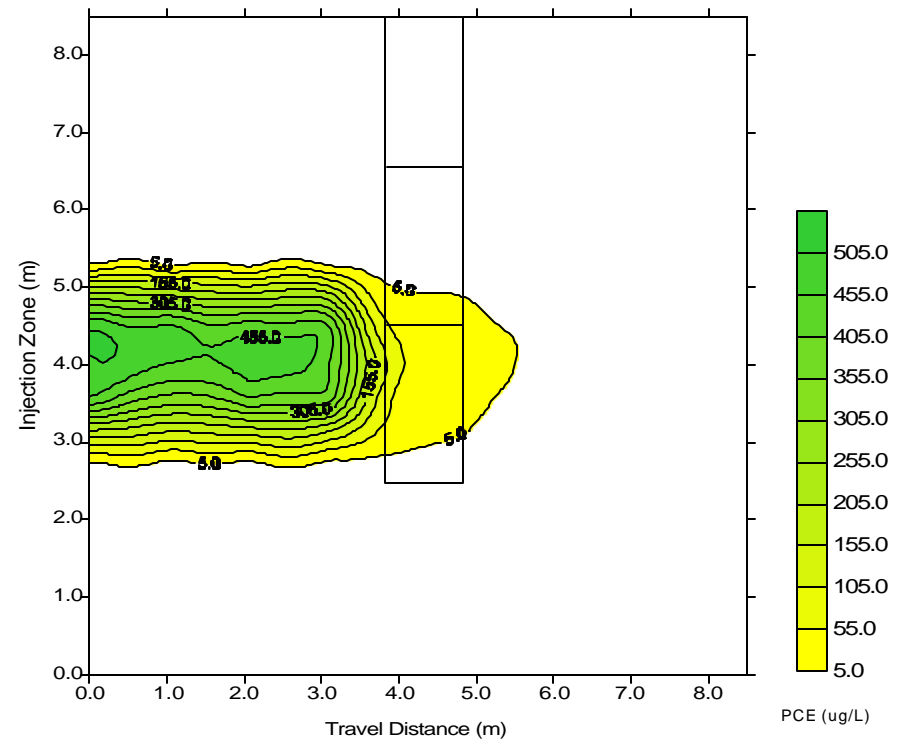


# Cr and PCE Distributions, 4<sup>th</sup> week

Cr Distribution after 26 days of injection (7/25/2001)  
Depth=1.0m  
Plan View

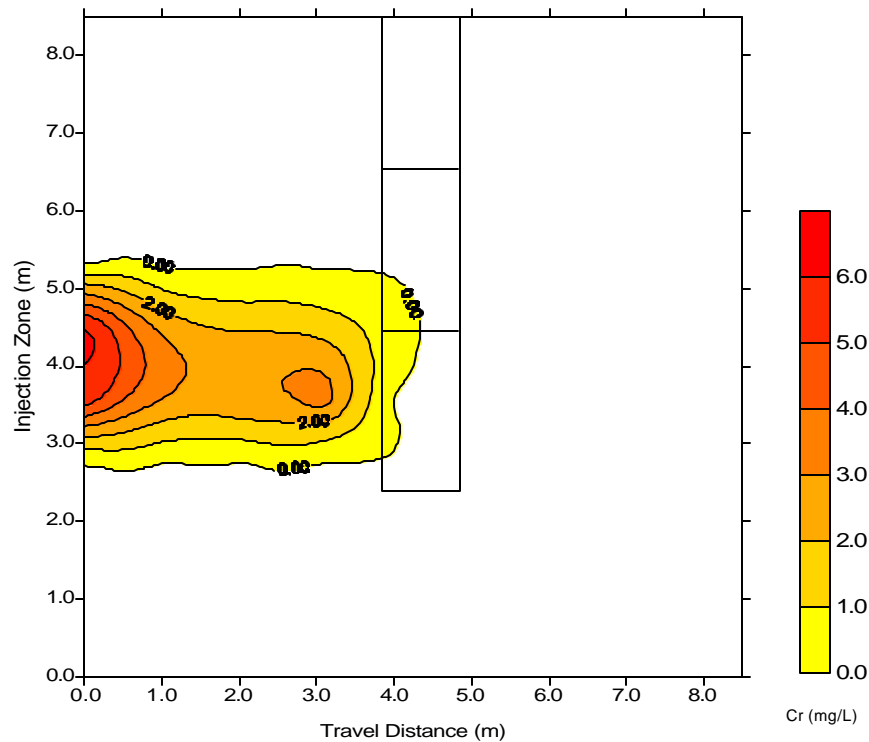


PCE Distribution after 29 days of injection (7/25/2001)  
Depth=1.0m  
Plan View

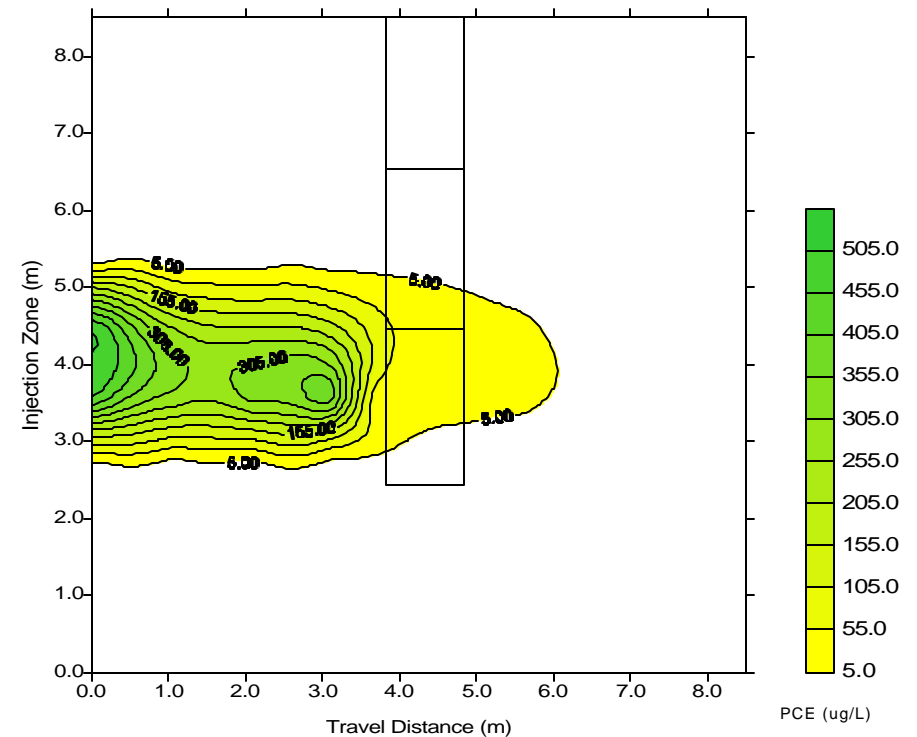


# Cr and PCE Distributions, 5<sup>th</sup> week

Cr Distribution after 33 days of injection (8/01/2001)  
Depth=1.0m  
Plan View



PCE Distribution after 36 days of injection (8/01/2001)  
Depth=1.0m  
Plan View



# Pilot Test vs. Lab Reduction Factors

(for a 1-m wide barrier)

Reduction Factor	PCE	$\text{CrO}_4^{2-}$
Lab R	1/10,000	>1/1000
Pilot Test R	1/100	>1/1000

# **Accomplishments of This Phase**

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## **DEVELOPED SMZ/ZVI PELLET TECHNOLOGY**

- **Simultaneously sorb/reduce contaminants**
- **Mechanically stable**
- **Highly permeable**

## **PILOT-TESTED SMZ/ZVI PERMEABLE BARRIER**

- **Barrier fully captured contaminant plume**
- **Chromate reduced below regulatory limits**
- **PCE reduced two orders of magnitude**

# Outline

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## PREVIOUS PROJECT PHASES

- Development of SMZ
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## CURRENT PROJECT PHASE

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# Schedule of Current Phase

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## TASK

## COMPLETION DATE

Optimize formulation

December 2000

Manufacture pellets

April 2001

Conduct pilot test

September 2001

Analyze results

October 2001

Topical Report

December 2001